

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
3 January 2003 (03.01.2003)

PCT

(10) International Publication Number
WO 03/000757 A1

- (51) International Patent Classification: **C08F 10/06**, 4/654, 4/651
- (21) International Application Number: PCT/EP02/06720
- (22) International Filing Date: 18 June 2002 (18.06.2002)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
01115000.0 20 June 2001 (20.06.2001) EP
- (71) Applicant (for all designated States except US): **BOREALIS POLYMERS OY** [FI/FI]; P.O. Box 330, FIN-06101 Porvoo (FI).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **DENIFL, Peter** [AT/AT]; Ritten 130, A-6156 Gries am Brenner (AT). **LEINONEN, Timo** [FI/FI]; Massatie 8, FIN-06750 Tolkkinen (FI).
- (74) Agent: **NOBBE, Matthias**; Vierung, Jentschura & Partner, Centroallee 263, 46047 Oberhausen (DE).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:**
- with international search report
 - before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PREPARATION OF OLEFIN POLYMERISATION CATALYST COMPONENT

(57) Abstract: A process for producing a Gp 2/transition metal olefin polymerisation catalyst component, in which a Gp 2 metal complex is reacted with a transition metal compound so as to produce an oil-in-oil emulsion, the disperse phase containing the preponderance of the Mg being solidified by heating to provide a catalyst component of excellent morphology. Polymerisation of olefins using a catalyst containing such a component is also disclosed. The process may be employed in the production of Ziegler-Natta catalysts.

WO 03/000757 A1

PREPARATION OF OLEFIN POLYMERISATION CATALYST COMPONENT

This invention relates to a process for the preparation of a particulate olefin polymerisation catalyst component, particularly one comprising a Gp 2 metal of the Periodic Table (IUPAC, Nomenclature of Inorganic Chemistry, 1989), a compound of a transition metal and an electron donor. The invention also relates to the use of such a catalyst component in the polymerisation of olefins.

10

Background of the invention

Processes for the preparation of such a catalyst component - as described, for instance, in WO 00/08073 and 00/08074 - usually include a step in which a magnesium-Gp 4 metal-electron donor component is recovered by precipitation from solution, typically by contacting the solution with a large amount of an aliphatic hydrocarbon. However, such precipitation leads to a tar-like reaction product of low catalytic activity, that needs to be washed several times in order to decrease the amount of inactive Gp IVB metal complex. Aromatic hydrocarbons have also been used for the precipitation, but they lead to a very finely divided precipitate which is difficult to deposit. Worse still, it is difficult to carry out such precipitation in a controlled and reproducible manner, leading to unsatisfactory product morphology. Moreover variable and low concentrations of catalyst constituents such as butyl chloride may result, as a consequence of precipitation evaporative removal of aliphatic solvent.

30

Description of the invention

We have devised a new technique for recovering such a component from solution, which avoids the unsatisfactory precipitation previously practised and leads to an improved

CONFIRMATION COPY

product morphology and consistent product composition.

According to the present invention a process for producing an olefin polymerisation catalyst component in the form of particles having a predetermined size range, comprises
5 preparing a solution of a complex of a Gp 2 metal and an electron donor by reacting a compound of said metal with said electron donor or a precursor thereof in an organic liquid reaction medium; reacting said complex, in solution, with a
10 compound of a transition metal to produce an emulsion the dispersed phase of which contains more than 50 mol% of the Gp 2 metal in said complex; maintaining the particles of said dispersed phase within the average size range 5 to 200 μm by agitation in the presence of an emulsion stabilizer and
15 solidifying said particles; and recovering, washing and drying said particles to obtain said catalyst component.

The compound of a transition metal is preferably a compound of a Group 4 metal. The Group 4 metal is preferably titanium, and
20 its compound to be reacted with the complex of a Gp 2 is preferably a halide. In a further embodiment of the invention a compound of a transition metal used in the process can also contain organic ligands typically used in the field known as a single site catalyst. In a still further embodiment of the
25 invention a compound of a transition metal can also be selected from Group 5 metals, Group 6 metals, Cu, Fe, Co, Ni and/or Pd. The complex of the Group 2 metal is preferably a magnesium complex. The invention will henceforth be described in relation to a preferred embodiment of the process, namely
30 to a process for the preparation of a Ziegler-Natta type catalyst.

A preferred embodiment of the invention is a process for producing catalysts of the Ziegler-Natta type, in the form of

particles having a predetermined size range, comprising:
preparing a solution of magnesium complex by reacting an
alkoxy magnesium compound and an electron donor or precursor
thereof in a C₆-C₁₀ aromatic liquid reaction medium; reacting
5 said magnesium complex with a compound of at least one IV
valent Gp 4 metal at a temperature greater than 10°C and less
than 60°C, to produce an emulsion of a denser, TiCl₄/toluene-
insoluble, oil dispersed phase having, Gp 4 metal/Mg mol ratio
0.1 to 10 in an oil disperse phase having Gp 4 metal/Mg mol
10 ratio 10 to 100; maintaining the droplets of said dispersed
phase within the size range 5 to 200 µm by agitation in the
presence of an emulsion stabilizer while heating the emulsion
to solidify said droplets; and recovering, washing and drying
the solidified particles to obtain said catalyst component.

15 The said disperse and dispersed phases are thus
distinguishable from one another by the fact that the denser
oil, if contacted with a solution of titanium tetrachloride in
toluene, will not dissolve in it. A suitable solution for
20 establishing this criterion would be one having a toluene mol
ratio of 0.1 to 0.3. They are also distinguishable by the fact
that the great preponderance of the Mg provided (as complex)
for the reaction with the Gp 4 metal compound is present in
the dispersed phase, as revealed by comparison of the
25 respective Gp 4 metal/Mg mol ratios.

In effect, therefore, virtually the entirety of the reaction
product of the Mg complex with the Gp 4 metal - which is the
precursor of the ultimate catalyst component - becomes the
30 dispersed phase, and proceeds through the further processing
steps to final dry particulate form. The disperse phase, still
containing a useful quantity of Gp 4 metal, can be reprocessed
for recovery of that metal.

The production of a two-phase, rather than single-phase (as in prior practice) reaction product is encouraged by carrying out the Mg complex/Gp 4 metal compound reaction at low temperature, specifically above 10°C but below 60°C, preferably between above 20°C and below 50°C. Since the two phases will naturally tend to separate into a lower, denser phase and supernatant lighter phase, it is necessary to maintain the reaction product as an emulsion by agitation in the presence of an emulsion stabiliser.

10

The resulting particles of the dispersed phase of the emulsion are of a size, shape (spherical) and uniformity which render the ultimate catalyst component extremely effective in olefin polymerisation. This morphology is preserved during the heating to solidify the particles, and of course throughout the final washing and drying steps. It is, by contrast, difficult to the point of impossibility to achieve such morphology through precipitation, because of the fundamental uncontrollability of nucleation and growth, and the large number of variables, which affect these events.

20

The electron donor is preferably an aromatic carboxylic acid ester, a particularly favoured ester being dioctyl phthalate. The donor may conveniently be formed in situ by reaction of an aromatic carboxylic acid chloride precursor with a C₂-C₁₆ alkanol and/or diol. The liquid reaction medium preferably comprises toluene.

25

Furthermore, emulsifying agents/emulsion stabilisers can be used additionally in a manner known in the art for facilitating the formation and/or stability of the emulsion. For the said purposes e.g. surfactants, e.g. a class based on acrylic or methacrylic polymers can be used. Preferably, said emulsion stabilizers are acrylic or methacrylic polymers, in

30

particular those with medium sized ester side chains having more than 10, preferably more than 12 carbon atoms and preferably less than 30, and preferably 12 to 20 carbon atoms in the ester side chain. Particular preferred are unbranched
5 C₁₂ to C₂₀ acrylates such as poly(hexadecyl)-methacrylate and poly(octadecyl)-methacrylate.

It has been found that the best results are obtained when the Gp 4 metal/Mg mol ratio of the denser oil is 1 to 5,
10 preferably 2 to 4, and that of the disperse phase oil is 55 to 65. Generally the ratio of the mol ratio Gp 4 metal/Mg in the disperse phase oil to that in the denser oil is at least 10.

Solidification of the dispersed phase particles by heating is
15 suitably carried out at a temperature of 70-150°C, usually at 90-110°C. Preparation of the magnesium complex may be carried out over a wide range of temperatures, 20 to 80°C being preferred, 50 to 70°C most preferred.

20 The finally obtained catalyst component is desirably in the form of particles having an average size range of 10 to 200 µm, preferably 20 to 50 µm.

The present invention further comprehends an olefin
25 polymerisation catalyst comprising a catalyst component prepared as aforesaid, in association with an alkyl aluminium cocatalyst, and optionally with external donors, and the use of that polymerisation catalyst for the polymerisation of C₂ to C₁₀-olefins.

30

The reagents can be added to the reaction medium in any order. However it is preferred that in a first step the alkoxy magnesium compound is reacted with a carboxylic acid halide precursor of the electron donor to form an intermediate; and

in a second step the obtained product is further reacted with the Gp 4 metal. The magnesium compound preferably contains from 1 to 20 carbon atoms per alkoxy group, and the carboxylic acid should contain at least 8 carbon atoms.

- 5 Reaction of the magnesium compound, carboxylic acid halide and polyhydric alcohol proceeds satisfactorily at temperatures in the range 20 to 80°C, preferably 50 to 70°C. The product of that reaction, the "Mg complex", is however reacted with the Gp 4 metal compound at a lower temperature, contrary to
10 previous practice, to bring about the formation of a two-phase, oil-in-oil, product.

Use of the aromatic medium for preparation of the Mg complex contributes to consistent product morphology and higher bulk
15 density. Catalyst bulk density and morphology correlate with product bulk density and morphology the so-called "replication effect".

The technique adopted in the novel regimen of the invention is
20 inherently more precise than that formerly employed, and thus further contributes to product consistency, as well as sharply reducing the volumes of solvent to be handled and thus improving process economics.

- 25 The reaction medium used as solvent can be aromatic or a mixture of aromatic and aliphatic hydrocarbons, the latter one containing preferably 5 - 9 carbon atoms, more preferably 5 - 7 carbon atoms, or mixtures thereof. Preferably, the liquid reaction medium used as solvent in the reaction is aromatic
30 and is more preferably selected from hydrocarbons such as substituted and unsubstituted benzenes, preferably from alkylated benzenes, even more preferably from toluene and the xylenes, and is most preferably toluene. The molar ratio of said aromatic medium to magnesium is preferably less than 10,

for instance from 4 to 10, preferably from 5 to 9.

- The recovered particulate product is washed at least once, preferably at least twice, most preferably at least three
- 5 times with a hydrocarbon, which preferably is selected from aromatic and aliphatic hydrocarbons, preferably with toluene, particularly with hot (e.g. 90°C) toluene. A further wash is advantageously performed with heptane, most preferably with hot (e.g. 90°C) heptane, and yet a further wash with pentane.
- 10 A washing step typically includes several substeps. A favoured washing sequence is, for example, one wash with toluene at 90°C, two washes with heptane at 90°C and one or two washes with pentane at room temperature.
- 15 The washing can be optimized to give a catalyst with novel and desirable properties. Finally, the washed catalyst component is dried, as by evaporation or flushing with nitrogen.

- It is preferable that the intermediates as well as the final
- 20 product of the process be distinct compounds with an essentially stoichiometric composition. Often, they are complexes. A complex is, according to Römpps Chemie-Lexicon, 7. Edition, Franckh'sche Verlagshandlung, W. Keller & Co., Stuttgart, 1973, page 1831, "a derived name of compounds of
- 25 higher order, which originate from the combination of molecules, - unlike compounds of first order, in the creation of which atoms participate".

- The alkoxy magnesium compound group is preferably selected
- 30 from the group consisting of magnesium dialkoxides, complexes of a magnesium dihalide and an alcohol, and complexes of a magnesium dihalide and a magnesium dialkoxide. It may be a reaction product of an alcohol and a magnesium compound selected from the group consisting of dialkyl magnesiums,

alkyl magnesium alkoxides, alkyl magnesium halides and magnesium dihalides. It can further be selected from the group consisting of dialkyloxy magnesiums, diaryloxy magnesiums, alkyloxy magnesium halides, aryloxy magnesium halides, alkyl
5 magnesium alkoxides, aryl magnesium alkoxides and alkyl magnesium aryloxides.

The magnesium dialkoxide may be the reaction product of a magnesium dihalide such as magnesium dichloride or a dialkyl
10 magnesium of the formula R_2Mg , wherein each one of the two Rs is a similar or different C_1 - C_{20} alkyl, preferably a similar or different C_4 - C_{10} alkyl. Typical magnesium alkyls are ethylbutyl magnesium, dibutyl magnesium, dipropyl magnesium, propylbutyl magnesium, dipentyl magnesium, butylpentylmagnesium,
15 butyloctyl magnesium and dioctyl magnesium. Most preferably, one R of the formula R_2Mg is a butyl group and the other R is an octyl group, i.e. the dialkyl magnesium compound is butyl octyl magnesium.

20 Typical alkyl-alkoxy magnesium compounds $RMgOR$, when used, are ethyl magnesium butoxide, butyl magnesium pentoxide, octyl magnesium butoxide and octyl magnesium octoxide.

Dialkyl magnesium, alkyl magnesium alkoxide or magnesium
25 dihalide can react with a polyhydric alcohol $R'(OH)_m$, or a mixture thereof with a monohydric alcohol $R'OH$.

Typical C_2 to C_6 polyhydric alcohols may be straight-chain or branched and include ethylene glycol, propylene glycol,
30 trimethylene glycol, 1,2-butylene glycol, 1,3-butylene glycol, 1,4-butylene glycol, 2,3-butylene glycol, 1,5-pentanediol, 1,6-hexanediol, 1,8-octanediol, pinacol, diethylene glycol, triethylene glycol, and triols such as glycerol, methylol propane and pentareythritol. The polyhydric alcohol can be

selected on the basis of the activity and morphology it gives the catalyst component.

The aromatic reaction medium may also contain a monohydric
5 alcohol, which may be straight- or branched-chain. Typical C₁-C₂₀ monohydric alcohols are methanol, ethanol, n-propanol, iso-propanol, n-butanol, iso-butanol, sec.butanol, tert.butanol, n-amyl alcohol, iso-amyl alcohol, sec.amyl alcohol, tert.amyl alcohol, diethyl carbinol, akt. amyl
10 alcohol, sec. isoamyl alcohol, tert.butyl carbinol. Typical C₆-C₁₀ monohydric alcohols are hexanol, 2-ethyl-1butanol, 4-methyl-2-pentanol, 1-heptanol, 2-heptanol, 4-heptanol, 2,4-dimethyl-3pentanol, 1-octanol, 2-octanol, 2-ethyl-1-hexanol, 1-nonanol, 5-nonanol, diisobutyl carbinol, 1-decanol and 2,7-
15 dimethyl-2-octanol. Typical >C₁₀ monohydric alcohols are n-1-undecanol, n-1-dodecanol, n-1-tridecanol, n-1-tetradecanol, n-1-pentadecanol, 1 -hexadecanol, n-1-heptadecanol and n-1-octadecanol. The monohydric alcohols may be unsaturated, as long as they do not act as catalyst poisons.

20

Preferable monohydric alcohols are those of formula R'OH in which R' is a C₂-C₆ alkyl group, most preferably a C₄-C₁₂ alkyl group, particularly 2-ethyl-1-hexanol.

25 Preferably, essentially all of the aromatic carboxylic acid ester is a reaction product of a carboxylic acid halide, preferably a dicarboxylic acid dihalide, more preferably an unsaturated α,β -dicarboxylic acid dihalide, most preferably phthalic acid dichloride, with the monohydric alcohol.

30

The compound of a four-valent Gp 4 metal compound containing a halogen is preferably a titanium tetrahalide. Equivalent to titanium tetrahalide is the combination of an alkoxy titanium

halide and a halogenation agent therefore, which are able to form a titanium tetrahalide *in situ*. The most preferred halide is the chloride, for zirconium and hafnium as well as for titanium.

5

The reaction conditions used in the claimed process may be varied according to the used reactants and agents.

As is known, the addition of at least one halogenated hydrocarbon during the process can lead to further improved catalytic activity. Reactive halogenated hydrocarbons preferably have the formula $R''X''_n$ wherein R'' is an n-valent C_1 - C_{20} hydrocarbyl group, particularly a C_1 - C_{10} paraffin, X'' is a halogen and n is an integer from 1 to 4.

15

Such chlorinated hydrocarbons include monochloromethane, dichloromethane, trichloromethane (chloroform), tetrachloromethane, monochloroethane, (1,1)-dichloroethane, (1,2)-dichloroethane, (1,1,1)-trichloroethane, (1,1,2)-trichloroethane, (1,1,1,2)-tetrachloroethane, (1,1,2,2)-tetrachloroethane, pentachloroethane, hexachloroethane, (1)-chloropropane, (2)-chloropropane, (1,2)-dichloropropane, (1,3)-dichloropropane, (1,2,3)-trichloropropane, (1)-chlorobutane, (2)-chlorobutane, isobutyl chloride, tert.butyl chloride, (1,4)-dichlorobutane, (1)-chloropentane, (1,5)-dichloropentane. The chlorinated hydrocarbons may also be unsaturated, provided that the unsaturation does not act as catalyst poison in the final catalyst component.

30 In the above formula, R'' is preferably a mono-or bivalent C_1 - C_{10} alkyl group, independently, X'' is preferably chlorine and, independently, n is preferably 1 or 2. Preferred compounds include butyl chloride ($BuCl$), dichloroalkanes such as (1,4)-dichlorobutane, and tertiary butyl chloride.

Though the catalyst preparation according to the inventive method can be carried out batchwise, it is also preferable and possible to prepare the catalyst component semi-continuously
5 our continuously. In such semi-continuous or continuous process, the solution of the complex of the Group 2 metal and said electron donor, which is prepared by reacting the compound of said metal with said electron donor in an organic liquid reaction medium, is mixed with at least one compound of
10 a transition metal, which might be solved in the same or different organic liquid reaction medium. The so obtained solution is then agitated, possibly in the presence of an emulsion stabilizer, and then the so-agitated emulsion is fed into a temperature gradient reactor, in which the emulsion is
15 subjected a temperature gradient, thus leading to solidifying the droplets of a dispersed phase of the emulsion.

When feeding said agitated emulsion to the temperature gradient reactor, an inert solvent, in which the droplets are
20 not soluble, can additionally be fed into that gradient reactor in order to improve the droplet formation and thus leading to a uniform grain size of the particles of the catalyst component, which are formed in the temperature gradient reactor when passing through said line. Such
25 additional solvent might be the same as the organic liquid reaction medium, which is used for preparing the solution of the complex of the Group 2 metal as explained above in more detail.

30 The solidified particles of the olefin polymerisation catalyst component can subsequently be recovered by an in-stream filtering unit and then, optionally after some additional washing and drying steps in order to remove unreacted starting components, can be stored for further use. In one embodiment

the catalyst can be fed after washing steps into the olefin polymerisation reactor, so that a continuous preparation and fed to the reactor is guaranteed.

- 5 As it can be seen from the above description of the semi-continuous or continuous process, it is thus possible to use separated reaction vessels for the different process steps and to transfer the reaction products which are prepared in the respective reaction vessels and to feed them in-line into
10 further reaction vessels for formation of the emulsion and, subsequently, of the solidified particles.

It is one possibility to use a full-continuous process as the time saving in said process is remarkable. In such fully
15 continuous process, the formation of the solidified particles could be carried out in the temperature gradient line in the kind of pipe reactor, which is sufficiently long and which is subjected said temperature gradient from the starting temperature in the lower range of 20 to 80°C up to a
20 "solidifying" temperature of 70 to 150°C. The temperature gradient is preferably obtained by means of heating the pipe reactor from the outside by applying normal heaters, microwaves, etc.

- 25 As mentioned before, a filtering unit might preferably be used for filtering the solidified particles from the solvent stream. For said filtering unit, various drums and sieving systems can be used, depending on the specific particle sizes.
- 30 Some preferred embodiments of the invention are described, by way of illustration, in the following Examples.

EXAMPLE 1

A magnesium complex solution was prepared by slowly adding

over a 40 minute period, with stirring, 110 ml of a 20% solution in toluene of BOMAG-A (Tradename) $[Mg(Bu)_{1.5}(Oct)_{0.5}]$ to 38.9 ml of 2-ethylhexanol which had been cooled to 5°C in a 300 ml glass reactor. During the addition the reactor contents were maintained below 15°C. The temperature was then raised to 60°C and held at that level for 30 minutes with stirring, at which time reaction was complete. 6.4 ml phthaloyl chloride was then added over an 11 minute period. The reactor contents were stirred at 60°C for 20 minutes, 12.9 ml 1-chlorobutane was added, and stirring continued for another 15 minutes at 60°C. The resulting stable, yellowish Mg complex solution was cooled to room temperature.

19.5 ml $TiCl_4$, 5 ml heptane and 28.7 of the above-prepared Mg complex solution were reacted at 25°C in a 300 ml glass reactor. After 5 minutes, reaction was complete and a dark red emulsion had formed. The temperature was raised to 50°C, 2 ml of Viscoplex 1-254 (Tradename) (40-44% of acrylic polymer in base oil) was added, and the reactor contents were stirred for 30 minutes. The resulting stabilized emulsion was then heated to 90°C, with stirring, for 10 minutes to solidify the particles forming the dispersed phase. After settling and syphoning the solids (2.6 grams) underwent washing with:

1. 100 ml toluene at 90°C for 30 minutes;
2. 60 ml heptane, at 90°C for 20 minutes;
3. 60 ml heptane, at 35°C for 10 minutes,
4. 60 ml pentane, at 30°C for 5 minutes; and
5. 60 ml pentane, at 30°C for 5 minutes.

The solids were then dried at 60°C by nitrogen purge. The particles were established by microscopic examination to be perfectly spherical in shape. The Coulter PSD is shown in Figure 1.

EXAMPLE 2

Example 1 was repeated, in order to evaluate the consistency of the procedure. The quantity of solids product was 2.6g, the particles perfectly spherical. The Coulter PSD is shown in Figure 2.

TABLE 1

Example	Ti%	Mg%	Dop%*	Coulter** 10 μ m	Coulter 50 μ m	Coulter 90 μ m
1	3.3	12.6	27.5	41.6	28	11.7
2	2.9	12.6	27.4	51.9	33.9	14.2

* Di-ethyl-hexyl phthalate (internal electron donor)

** Measured with Coulter LS200 at room temperature with n-heptane as medium

EXAMPLES 3 and 4

The products of Examples 1 and 2 were evaluated as catalyst components in propylene polymerisation in the following manner.

0.9 ml triethyl aluminium (TEA) (co-catalyst), 0.12 ml cyclohexyl methyl dimethoxy silane (CMMS) as an external donor and 30 ml n-pentane were mixed and allowed to react for 5 minutes. Half of the mixture was then added to a polymerisation reactor and the other half was mixed with 20 mg of the components prepared in Examples 1 and 2. After an additional 5 minutes the component TEA/donor/n-pentane mixture was added to the reactor. The Al/Ti mole ratio of the resulting polymerisation catalyst was 250 mol/mol and the Al/CMMS mole ratio was 10 mol/mol.

Propylene bulk polymerisation was carried out in a stirred 5 l

tank reactor.

70 mmol hydrogen and 1400 g propylene were introduced into the reactor and the temperature was raised within 15 minutes to the polymerisation temperature of 70°C. The polymerisation time at 70°C was 60 minutes, after which the polymer formed was taken out from the reactor. Example 3 employed the catalyst containing component of Example 1 and Example 4 that of Example 2.

10

The results of the polymerisation evaluations are summarised in the following Table 2.

TABLE 2

Example	Activity kgPP/gCat	MFR ¹ g/10min	XS ² %	BD ³ g/ml	% particles <0.1mm
3	24.1	5.5	1.7	0.45	0
4	24.4	4.1	1.4	0.44	0

15

¹ ISO 1133, 2.16 kg load at 230°C

² xylene-soluble fraction of product at 25°C

³ polymer-bulk density (ASTM D 1895)

20 The polymer particles were spherical, with a markedly narrow size distribution: more than 75% of the product was of 0.5-1.00 mm particle diameter.

Examples 5 - 8

25 In following examples poly(hexadecylmethacrylate) in different amounts (Examples 5 - 7) and poly(octadecylmethacrylate) (Example 8), both available from Aldrich, were used in stead of Viscoplex.

Preparation of the soluble Mg-complexes

Method A)

In a 150 l steel reactor 19,4 kg of 2-ethyl hexanol were added at 20 °C. 56,0 kg of a 20 % BOMAG A solution in toluene were then slowly added to the well stirred alcohol. The temperature of the mixture was then increased to 60 °C, and the reactants were allowed to react for 30 minutes at this temperature. After addition of 5,5 kg of 1,2-phthaloyl dichloride, the reaction mixture was stirred at 60 °C for another 30 minutes to ensure complete reaction. 13.8 kg of 1-chloro butane were then added at 60 °C, and stirring at this temperature was continued for 30 minutes. After cooling to room temperature a yellow solution was obtained.

Method B)

In a 300 ml glass reactor 38,9 ml of 2-ethyl hexanol were added at 20 °C. 110,0 ml of a 20 % BOMAG A solution in toluene were then slowly added to the well stirred alcohol. The temperature of the mixture was then increased to 60 °C, and the reactants were allowed to react for 60 minutes at this temperature. After addition of 6,4 ml of 1,2-phthaloyl dichloride, the reaction mixture was stirred at 60 °C for another 60 minutes to ensure complete reaction. After cooling to room temperature a yellow solution was obtained.

25

Example 5

Preparation of the catalyst component

19,5 ml titanium tetrachloride were placed in a 300 ml glass reactor equipped with a mechanical stirrer. After addition of 5,0 ml n-heptane, 31,0 g of the Mg-complex (method A) was added to the well-stirred reaction mixture at 25 °C. Mixing speed was kept constant 170 rpm through whole synthesis. After addition a dark red emulsion was formed. The temperature was

increased to 50 °C and 0,9 ml poly(hexadecyl methacrylate)-toluene solution was added. After 30 min mixing, the temperature was increased to 90 °C and then after 10 min the mixing was stopped and the catalyst was let to settle. After
5 siphoning, the solid was washed with 100 ml of toluene at 90 °C for 30 min. Then the washings were continued with two times 60 ml heptane and twice with 60 ml pentane. The first heptane washing took 20 min at 90 °C and the second one 10 min. During
10 the second heptane wash the temperature was decreased down to c. 25 °C. The pentane washing was then carried out for 5 min at c. 25 °C.

Finally the solid catalyst was dried at 60 °C by purging nitrogen through the catalyst bed.

Catalyst composition is shown in TABLE 3.

The catalyst particle size distribution by Coulter is shown in Figure 3.

Bulk polymerisation of propylene

20 The propylene bulk polymerisation was carried out as in Example 3 but using the catalyst of example 5.

Polymerisation results are disclosed in TABLE 4.

25 Polymer particle size distribution by sieving is disclosed in TABLE 5.

Example 6

30 The catalyst preparation and polymerisation were carried out as in the Example 5, except 0,45 ml poly(hexadecyl methacrylate)-toluene solution was used in catalyst preparation.

Catalyst composition is disclosed in TABLE 3 and

35 polymerisation results in TABLE 4 and polymer particle size distribution in TABLE 5.

The catalyst particles were spherical and catalyst particle size distribution by Coulter is shown in Figure 4.

Example 7

- 5 The catalyst preparation and polymerisation were carried out as in the Example 5, except 1,35 ml poly(hexadecyl methacrylate)-toluene solution was used in catalyst preparation. Catalyst composition is disclosed in TABLE 3 and polymerisation results in TABLE 4 and polymer particle size distribution in TABLE 5.
- 10 The catalyst particles were spherical.
- The catalyst particle size distribution by Coulter is shown in Figure 5.

Example 8

- 15 Example 8 was done as Example 5, but Mg complex (method B) was used and the poly(octadecyl methacrylate)-toluene solution was used instead of poly(hexadecyl methacrylate).
- 20 The catalyst particles were spherical. Catalyst composition is disclosed in TABLE 3 and polymerisation results in TABLE 4 and polymer particle size distribution in TABLE 5. The catalyst particle size distribution by Coulter is shown in Figure 6.

25

TABLE 3 - Catalyst composition

Example	Ti%	Mg%	Cl%	DOP%
5	2,7	11,0	40,1	27,1
6	2,8	14,5	50,6	27,4
7	2,8	12,7	45,4	27,5
8	3,2	13,4	48,6	26,8

TABLE 4 - Polymerisation results

Example	Activity kgPP/gCat	MFR g/10min	XS %	BD G/ml
5	34,4	6,2	2,3	0,42
6	31,1	6,5	2,3	0,43
7	21,1	7,0	2,5	0,44
8	39,5	4,7	1,8	0,40

TABLE 5. Polymer particle size distribution by sieving.**% Polymer on sieves**

Example	4 mm	2 mm	1 mm	0,5 mm	0,18 mm	0,1 mm	0,056 mm	pan
5	0,7	24,7	56,9	14,2	3,2	0,2	0	0
6	6,1	43,1	31,4	16,7	2,8	0,1	0	0
7	1,1	35,0	37,7	24,5	1,4	0,2	0	0
8	16,7	54,4	18,9	9	0,7	0,1	0,1	0

5

CLAIMS

1. A process for producing an olefin polymerisation catalyst component in the form of particles having a predetermined size range, comprising:
- 5 preparing a solution of a complex of a Gp 2 metal and an electron donor by reacting a compound of said metal with said electron donor or a precursor thereof in an organic liquid reaction medium,
- 10 reacting said complex, in solution, with at least one compound of a transition metal to produce an emulsion the dispersed phase of which contains more than 50 mol% of the Gp 2 metal in said complex;
- maintaining the droplets of said dispersed phase
- 15 within the average size range 5 to 200 μm by agitation in the presence of an emulsion stabilizer and solidifying said droplets; and
- recovering, washing and drying said particles to obtain said catalyst component.
- 20
2. A process according to claim 1 wherein said transition metal is a Gp 4 metal.
3. A process according to claim 1 or claim 2 wherein said
- 25 Gp 2 metal is magnesium.
4. A process according to any preceding claim wherein said organic liquid reaction medium comprises a C₆-C₁₀ aromatic hydrocarbon or a mixture of C₆-C₁₀ aromatic
- 30 hydrocarbon and C₅ - C₉ aliphatic hydrocarbons.
5. A process according to any preceding claim wherein said emulsion is composed of a dispersed phase which is a TiCl₄/toluene-insoluble oil having a Gp 4 metal/Mg mol

ratio greater than 0.1 and less than 10 and a disperse phase which is an oil less dense than that of the dispersed phase and which has a Gp 4 metal/Mg mol ratio of 10 to 100.

5

6. A process according to claim 5 wherein the Gp 4 metal/Mg mol ratio of said disperse phase is 20 to 80.

10

7. A process according to claim 5 wherein the Gp 4 metal/Mg mol ratio of said disperse phase is 45 to 75.

15

8. A process according to any preceding claim wherein said complex and said transition metal compound are reacted at a temperature of 10 to 60°C.

20

9. A process according to any preceding claim wherein the solidification of said particles is effected by heating.

10. A process according to any preceding claim wherein said electron donor is an aromatic carboxylic acid ester.

11. A process according to any preceding claim wherein said electron donor is di(ethyl-hexyl) phthalate.

25

12. A process according to any preceding claim wherein said electron donor is formed in situ by reaction of an aromatic carboxylic acid chloride precursor with a C₂-C₁₆ alkanol and/or diol.

30

13. A process according to any preceding claim wherein said liquid reaction medium comprises toluene.

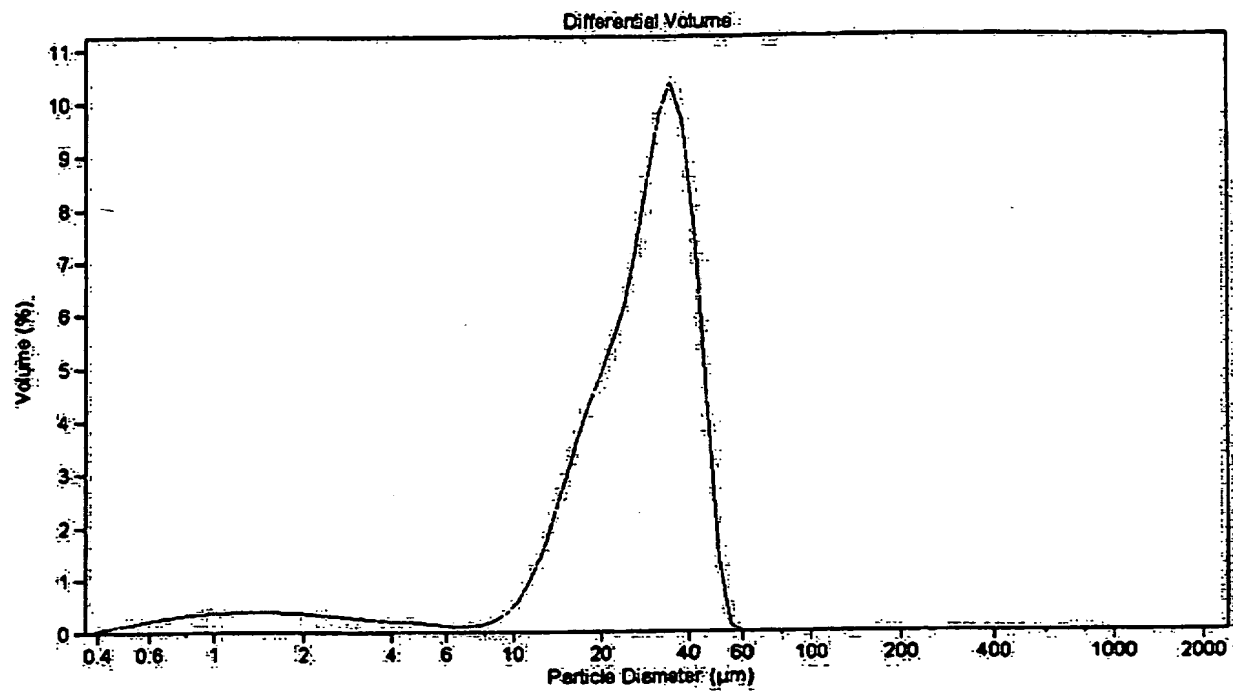
14. A process according to any of claims 2 to 13 wherein said Gp 4 metal is titanium.

15. A process according to any of claims 2 to 14 wherein said compound of a Gp 4 metal is a halide.
- 5 16. A process according to any of claims 3 to 15 wherein said magnesium complex and Gp 4 metal compound are reacted at a temperature of greater than 20°C to less than 50°C.
- 10 17. A process according to any preceding claim wherein said emulsion stabilizer is a surfactant.
18. A process according to claim 17 wherein said surfactant comprises an acrylic or methacrylic polymer.
- 15 19. A process according to any of claims 5 to 18 wherein the Gp 4 metal/Mg mol ratio of said denser oil is 2 to 4 and that of the disperse phase oil is 55 to 65.
- 20 20. A process according to claim 19 wherein the ratio of the mol ratio Gp 4 metal/Mg in the disperse phase oil to that in said denser oil is at least 10.
- 25 21. A process according to any of claims 8 to 20 wherein the emulsion is heated to a temperature of 70-150°C to solidify said particles.
22. A process according to claim 21 wherein the temperature to which the emulsion is heated is 90-110°C.
- 30 23. A process according to any preceding claim wherein the preparation of the Gp 2 metal complex is carried out at a temperature of 20 to 80°C.

24. A process according to 23 wherein the Gp 2 metal is magnesium and the preparation of the magnesium complex is carried out at a temperature of 50 to 70°C.
- 5 25. A process according to claim 1 wherein said transition metal is a Gp 5 metal and/or a Gp 6 metal.
26. A process according to claim 1 wherein said transition metal is Cu, Fe, Co, Ni and/or Pd.
- 10 27. A process according to any preceding claim wherein said obtained catalyst component is in the form of particles having an average size range of 5 to 200µm.
- 15 28. A process according to claim 27 wherein said particles have an average size range of 10 to 100 µm, preferably 20 to 50 µm.
- 20 29. An olefin polymerisation catalyst comprising a catalyst component prepared according to any of claims 1 to 28 and an alkylaluminium cocatalyst and optionally an external donor
- 25 30. Use of a catalyst in accordance with claim 29 for the polymerisation of C₂ to C₁₀ α-olefins.

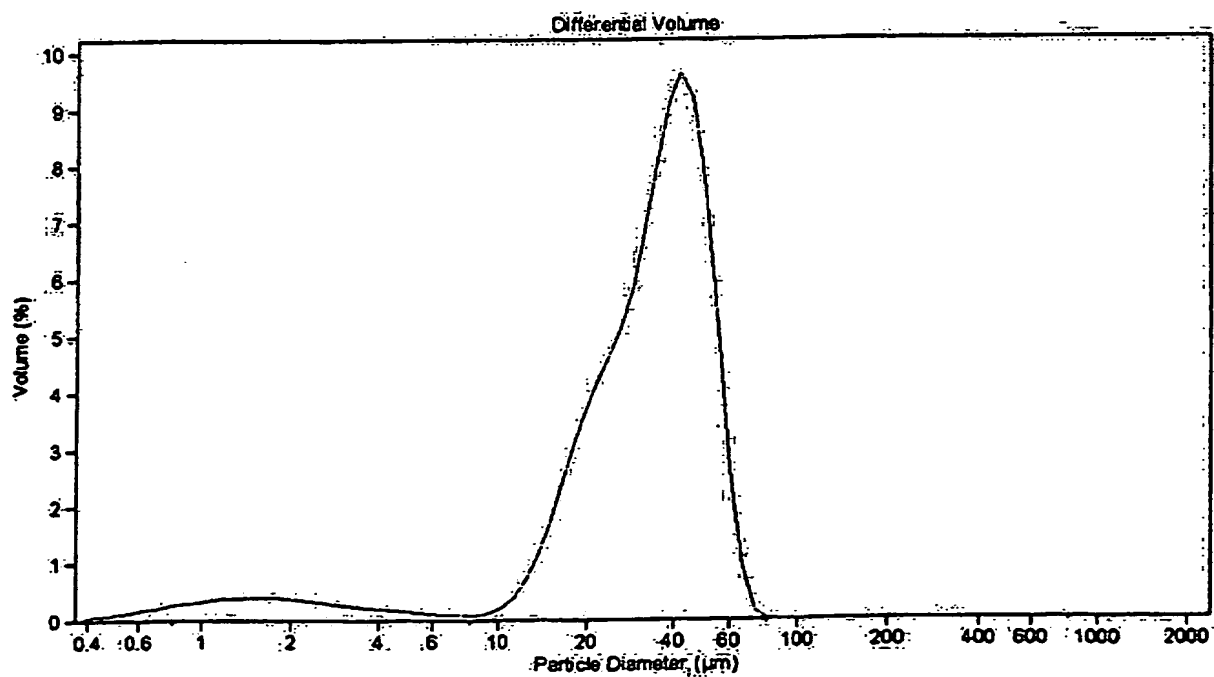
1 / 3

Figure 1



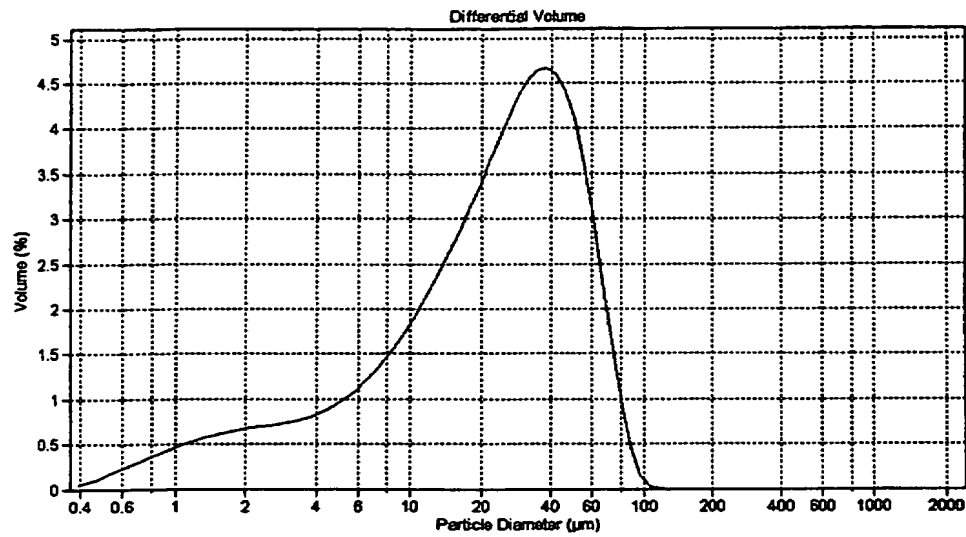
5

Figure 2



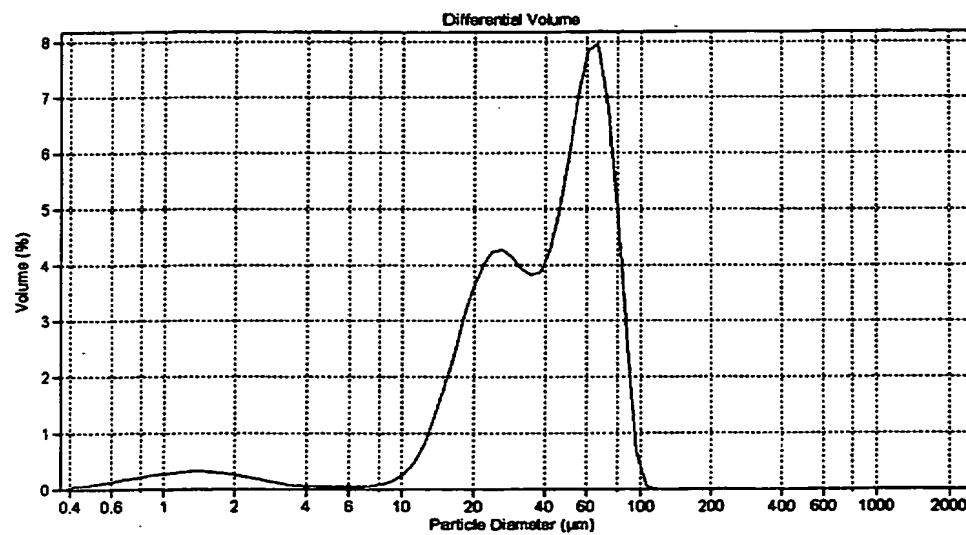
2 / 3

Figure 3



5

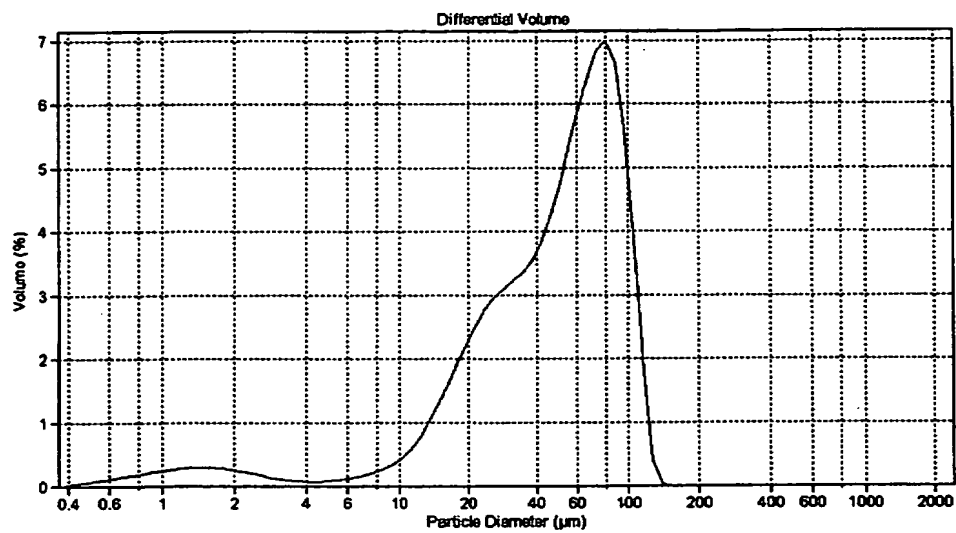
Figure 4



10

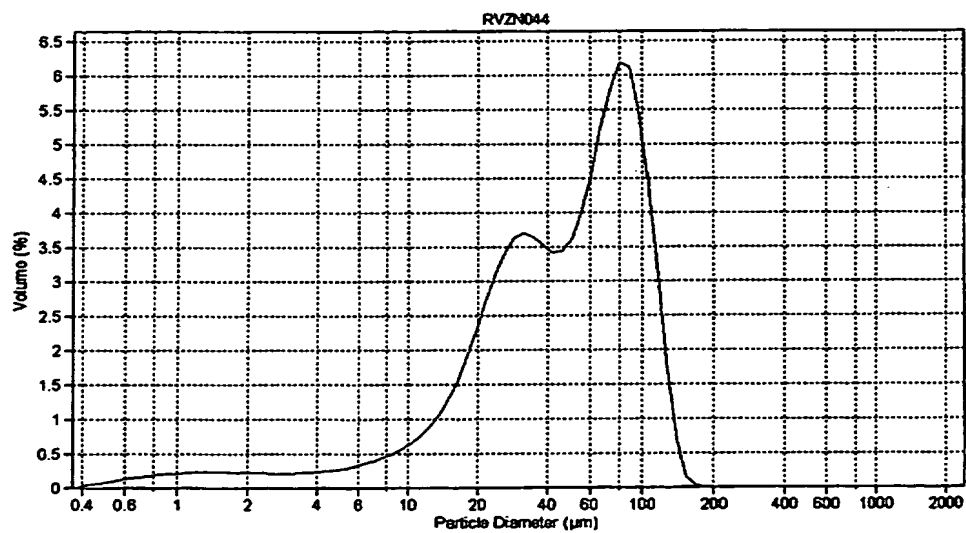
3 / 3

Figure 5



5

Figure 6



10

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 02/06720

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08F10/06 C08F4/654 C08F4/651

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 083 074 A (MONTEDISON SPA) 6 July 1983 (1983-07-06) page 16 -page 17; examples 9-15 page 29 -page 30; example 21 claims 1,6-10	1
A	EP 0 255 790 A (MONTEDISON SPA) 10 February 1988 (1988-02-10) example 1 claim 1	1
A	EP 0 536 840 A (ENICHEM POLIMERI) 14 April 1993 (1993-04-14) examples 6,7 claim 1	1

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *8* document member of the same patent family

Date of the actual completion of the international search

17 October 2002

Date of mailing of the international search report

24/10/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl
Fax (+31-70) 340-3016

Authorized officer

Gamb, V

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/06720

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0083074	A	06-07-1983	IT 1169291 B	27-05-1987
			AT 47404 T	15-11-1989
			AU 565828 B2	01-10-1987
			AU 9169382 A	30-06-1983
			BR 8207449 A	18-10-1983
			CA 1195680 A1	22-10-1985
			DE 3279988 D1	23-11-1989
			EP 0083074 A1	06-07-1983
			ES 518515 D0	01-06-1986
			ES 8607345 A1	01-11-1986
			GR 78407 A1	27-09-1984
			IN 161918 A1	27-02-1988
			IN 158358 A1	25-10-1986
			JP 1804180 C	26-11-1993
			JP 4080045 B	17-12-1992
			JP 58113211 A	06-07-1983
			KR 9002359 B1	12-04-1990
			NO 824222 A ,B,	27-06-1983
			SU 1545943 A3	23-02-1990
			US 4517307 A	14-05-1985
			ZA 8209392 A	30-11-1983
EP 0255790	A	10-02-1988	IT 1213474 B	20-12-1989
			IT 1213541 B	20-12-1989
			CA 1293588 A1	24-12-1991
			DE 3765351 D1	08-11-1990
			EP 0255790 A1	10-02-1988
			JP 63113004 A	18-05-1988
			US 4804798 A	14-02-1989
EP 0536840	A	14-04-1993	IT 1251679 B	19-05-1995
			AT 131837 T	15-01-1996
			AU 661043 B2	13-07-1995
			AU 2617192 A	22-04-1993
			BR 9203928 A	27-04-1993
			CA 2080147 A1	10-04-1993
			CN 1071669 A ,B	05-05-1993
			DE 69206945 D1	01-02-1996
			DE 69206945 T2	20-06-1996
			DK 536840 T3	26-02-1996
			EG 20447 A	29-04-1999
			EP 0536840 A1	14-04-1993
			ES 2081037 T3	16-02-1996
			FI 924517 A	10-04-1993
			GR 3018747 T3	30-04-1996
			JP 5214025 A	24-08-1993
			KR 9512095 B1	14-10-1995
			MX 9205770 A1	01-05-1993
			NO 923905 A ,B,	13-04-1993
			RU 2091392 C1	27-09-1997
			US 5320995 A	14-06-1994
			ZA 9207687 A	05-05-1993